

## ELECTROPHILIC SUBSTITUTION AT A SATURATED CARBON ATOM VI. DETERMINATION OF THE POLARITY "X" OF DIMETHYL SULFOXIDE AND ACETONITRILE BY THE KINETIC STUDY OF IODODEMETALLATION OF TETRAALKYL TIN AND -LEAD COMPOUNDS

M. GIELEN\* AND J. NASIELSKI\*\*

*Faculté des Sciences, Service de Chimie Organique, Université Libre de Bruxelles (Belgium)*

(Received May 1st, 1966)

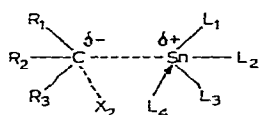
### INTRODUCTION

The announcement of a forthcoming publication<sup>1</sup> on the kinetics of the iododemetalation of organolead compounds<sup>2</sup> prompts us to disclose a series of results on the same subject.

Only a few kinetic studies of aliphatic electrophilic substitution performed on tetraalkyllead compounds are described in the literature; the protodemetalation of some  $R_4Pb$  compounds by acetic acid and perchloric acid in the same solvent has been examined by Robinson<sup>4</sup>.

Study of the kinetics of the reaction between iodine<sup>3</sup> or bromine<sup>5</sup> and tetraalkylleads in methanol led us to emphasize the close analogy existing between reactions on organotin and organolead compounds.

A thorough analysis of the iododemetalation of mixed organotin compounds ( $R_3SnR'$ )<sup>6</sup> has shown that the bond-breaking of the carbon-tin bond is the rate-determining factor. Consequently, any factor that will stabilize the incipient negative



charge on carbon ( $R_1$ ,  $R_2$ ,  $R_3$  and  $X_2$ ) or stabilize the partial positive charge on tin ( $L_1$ ,  $L_2$ ,  $L_3$  and  $L_4$ \*\*\*) in the transition state will accelerate the reaction.

We have already proposed eqn. (1) to describe more quantitatively the effect of solvents on the rate of aliphatic electrophilic reactions<sup>7</sup>.

$$\log k/k_0 = p \cdot X \quad (1)$$

$k$  is the rate constant of an electrophilic aliphatic substitution reaction on an organometallic compound in a given solvent

\* Chargé de Recherches du F.N.R.S.

\*\* Associé du F.N.R.S.

\*\*\*  $L_4$  is generally a solvent molecule, when it is nucleophilic enough; when not,  $L_4$  may be  $X_2$ .

$k_0$  is the rate constant of the same reaction, on the same organometallic compound, in acetic acid

$p$  is a constant depending on the nature of the electrophile and on the organometallic compound ( $p$  has been set equal to 1.00 for the bromodemetalation of tetramethyltin)

$X$  is defined as the "polarity of the solvent"

This relationship yields the values  $X = -4.8$  for carbon tetrachloride,  $-1.9$  for chlorobenzene,  $0.00$  for acetic acid and  $0.9$  for methanol.

We also showed that there is a linear relationship between the ratio  $k(\text{Me})/k(\text{Et})$  and the polarity " $X$ " of the solvent. For the bromodemetalation of tetraalkyltins, this is expressed by eqn. (2) while, for the iododemetalation of the same compounds, one finds eqn. (3).

$$\log [k(\text{Me})/k(\text{Et})]_{\text{Sn}}^{\text{Br}} = 0.47 X - 0.04 \quad (2)$$

$$\log [k(\text{Me})/k(\text{Et})]_{\text{Sn}}^{\text{I}} = 0.61 X + 0.4 \quad (3)$$

#### IODODEMETALLATION OF $\text{R}_4\text{Sn}$ IN DMSO

The study of the iododemetalation of tetraalkyltins has been extended to another solvent: dimethyl sulfoxide (DMSO) in order to determine its polarity " $X$ ". The rate equation has been found to be

$$v = k'_2 [M] [I_2]$$

where  $[M]$  stands for the concentration of  $\text{R}_4\text{Sn}$ .

Typical results are summarized in Table 1 and allow us to calculate  $k(\text{Me})/k(\text{Et})$  for this reaction in this particular solvent.

TABLE 1

IODODEMETALLATION OF  $\text{Me}_4\text{Sn}$  AND  $\text{Et}_4\text{Sn}$  IN DMSO

$D_0 = \varepsilon(I_2) \cdot [I_2]_0$ ,  $\varepsilon(I_2) = 4950$  at  $390 \text{ m}\mu$ ;  $t = 20.0^\circ$

$M$	$[M] \cdot 10^2$	$D_0$	$k'_2$ ( $l \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$ )
$\text{Me}_4\text{Sn}$	2.11	1.34	$0.48 \pm 0.01$
$\text{Et}_4\text{Sn}$	7.70	1.53	$0.021 \pm 0.001$
$\text{Et}_4\text{Sn}$	11.3	2.17	$0.021 \pm 0.001$
$\text{Et}_4\text{Sn}$	11.4	2.10	$0.020 \pm 0.001$

Since the equilibrium ( $K'$ ):  $I_2 + \text{DMSO} \rightleftharpoons I_2 \cdot \text{DMSO}$  causes a reduction in the concentration in free iodine<sup>8</sup>, which is different from that ( $K''$ ) caused by acetic acid:  $I_2 + \text{AcOH} \rightleftharpoons I_2 \cdot \text{AcOH}$ , one must expect eqn. (1) not to be applicable to give a correct value for  $X$  (DMSO), because the ratio of  $k'_2$ 's in different solvents is not equal to the ratio of the real  $k_2$ 's.

This disturbing influence of  $K'$  can be eliminated by using the ratio  $k(\text{Me})/k(\text{Et})$  [eqn. (3)] for the determination of  $X$  [instead of eqn. (1)], since

$$\frac{k'_2(\text{Me})}{k'_2(\text{Et})} \equiv \frac{k_2(\text{Me}) \cdot f(K')}{k_2(\text{Et}) \cdot f(K')} = \frac{k_2(\text{Me})}{k_2(\text{Et})}$$

Eqn. (3) is thus quite convenient for the determination of the polarity "X" of DMSO; in this way, one finds  $X(\text{DMSO}) = 1.6$ .

DMSO turns out to be by far the most polar of all the solvents studied up to now for this type of reactions. This observation is not surprising, since DMSO shows the highest dielectric constant ( $D = 45$ )<sup>9</sup> and the strongest nucleophilicity towards tin ( $\Delta J = 12$ )<sup>10</sup>.

#### IODODEMETALLATION OF $R_4Pb$ IN METHANOL, ACETIC ACID AND DIMETHYL SULFOXIDE IN THE PRESENCE OF IODIDE IONS

The study of the solvent effect on electrophilic substitutions at a saturated carbon atom has been extended to the iododemetalation<sup>3</sup> of tetraalkylleads<sup>11</sup> in methanol, acetic acid and dimethyl sulfoxide.

TABLE 2

#### IODODEMETALLATION OF TETRAALKYLLEADS

In  $\text{MeOH} \cdot \text{I}^-$ ,  $\epsilon(\text{I}_3^-) = 26,800$  at  $365 \text{ m}\mu$ ; in  $\text{AcOH} \cdot \text{I}^-$ ,  $\epsilon(\text{I}_3^-)$  at  $432 \text{ m}\mu^a$ ; and in  $\text{DMSO} \cdot \text{I}^-$ ,  $\epsilon(\text{I}_3^-) = 12,200$  at  $385 \text{ m}\mu$ .

<i>M</i>	$[M] \cdot 10^2$	$D_o$	<i>Solvent</i>	$k_{\text{exp}}$ at 20° ( $l \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$ )	<i>Ref.</i>
$\text{Me}_4\text{Pb}$	0.0076	0.547	MeOH	5.1	3
	0.0113	0.554	NaI 0.1 M	5.1	3
	0.0189	0.557		5.1	3
	0.0282	0.556		5.2	3
	0.0204	0.380		5.3	3
	0.0329	1.61		5.3	
	0.0662	1.60		5.0	
	0.114	1.55		5.1	
$\text{Et}_4\text{Pb}$	0.0518	1.60	MeOH	1.81	
	0.0687	2.15	NaI 0.1 M	1.80	
	0.0884	1.70		1.79	
	0.1097	1.90		1.81	
	0.426	1.50		1.80	
	0.427	1.20		1.80	
$\text{Me}_4\text{Pb}$	2.140	1.60	AcOH <sup>a</sup>	1.16	
$\text{Et}_4\text{Pb}$	1.777	1.23	NaI 0.1 M	0.657	
$\text{Me}_4\text{Pb}$	1.036	1.45	DMSO	0.353	
	1.536	2.90	NaI 0.1 M	0.383	
	2.040	2.00		0.356	
$\text{Et}_4\text{Pb}$	1.053	1.52	DMSO	0.084	
	2.420	1.000	NaI 0.1 M	0.088	

<sup>a</sup> The value of  $\epsilon(\text{I}_3^-)$  in acetic acid is very difficult to measure, because dissolution of iodide ions in that solvent is always accompanied by the formation of small quantities of iodine. For a pseudo-unimolecular reaction, it is not necessary to know  $\epsilon$  in order to evaluate  $k_{\text{exp}}$  and this value has not been determined. Robinson<sup>4</sup> has shown that one hour is necessary to acetolyse only 3% of  $R_4Pb$ ; since our runs are completed within ten minutes, they are not affected by this slow protodemetalation.

TABLE 3

INFLUENCE OF  $[I^-]$  ON  $k_{\text{exp}} \cdot [I^-]$  FOR IODODEMETHALLATION OF TETRAMETHYLLEAD IN METHANOL AND DIMETHYL SULFOXIDE<sup>a</sup>

Ionic strength:  $\mu = 0.715$  in methanol and  $\mu = 0.100$  in DMSO.

Solvent	$[M] \cdot 10^2$	$[I^-]$	$D_0$	$k_{\text{exp}}^{20^\circ}$	$k_{\text{exp}} \cdot [I^-]$	Ref.
MeOH	0.241	0.015	0.80	55.8	0.84	3
	2.04	0.115	0.56	7.21	0.83	3
	4.13	0.215	0.75	3.89	0.84	3
DMSO <sup>b</sup>	0.239	0.0101	0.98	3.81	0.0385	
	0.230	0.0101	2.80	3.79	0.0383	
	0.57	0.0202	5.07	1.91	0.0385	
	1.54	0.100	2.90	0.38	0.0383	
	2.04	0.100	2.00	0.36	0.0356	

<sup>a</sup> The reaction of iodine with tetramethyllead is very fast in acetic acid, even when  $[I^-] = 0.1 M$  and the influence of  $[I^-]$  on  $k_{\text{exp}} \cdot [I^-]$  could not be ascertained in this solvent. <sup>b</sup> Because DMSO is very hygroscopic, it was advisable to determine the influence of water on the rate constant  $k_{\text{exp}}$ . The addition of 0.39 mole/l of  $H_2O$  causes a very slight increase of  $k_{\text{exp}}$  from 0.38 to 0.40;  $k_{\text{exp}}$  is equal to 0.46 when  $[H_2O] = 1 M$ . These small variations of the rate constant with increasing concentrations of water allow us to trust our experimental results in DMSO, even without having measured the water concentration for each run.

The results are summarized in Table 2

The rate law  $v = k_{\text{exp}} \cdot [M][I_3^-]$  allows the determination of an experimental constant which contains the equilibrium constant  $K$  of  $I_2 + I^- \rightleftharpoons I_3^-$ .

Here again, one can eliminate the disturbing influence of  $K$  by examining the ratio  $k(\text{Me})/k(\text{Et})$

$$\frac{k_{\text{exp}}(\text{Me})}{k_{\text{exp}}(\text{Et})} = \frac{k_2(\text{Me}) \cdot f(K)}{k_2(\text{Et}) \cdot f(K)} = \frac{k_2(\text{Me})}{k_2(\text{Et})}$$

With the results obtained in methanol and acetic acid, it is possible to establish an equation, analogous to eqn. (3), relating  $\log k(\text{Me})/k(\text{Et})$  to  $X$ , and one finds

$$\log [k(\text{Me})/k(\text{Et})]_{\text{Pb}}^{\text{I}_2} = 0.225 X + 0.245 \quad (4)$$

and inserting the experimental value (4.24) for  $[k(\text{Me})/k(\text{Et})]_{\text{Pb}}^{\text{I}_2}/\text{DMSO} \cdot I^-$  yields directly  $X = 1.65$  for that solvent.

This value agrees well with  $X = 1.6$  obtained for DMSO through the same reaction performed on tetraalkyltins.

#### IODODEMETALLATION OF $R_4\text{Pb}$ IN $\text{MeCN} \cdot I^-$

The same reaction has been examined in a very poorly nucleophilic and poorly electrophilic solvent, namely acetonitrile ( $\text{MeCN}$ ). Its nucleophilicity towards tin is indeed equal to that of acetic acid, as shown by the values of  $\Delta J$  observed in both solvents<sup>7</sup>, its acidity being of course much less than that of acetic acid.

The observed rate law  $v = k_{\text{exp}} [M][I_3^-]$  can be a superposition of three distinct mechanisms<sup>3</sup>

$$v = k_2[M][I_2], v = k_1[M][I_3^-] \text{ and } v = k_3[M][I_2][I^-];$$

and it can be shown<sup>12</sup> that  $[I^-] \cdot k_{\text{exp}} = k_2/K + (k_1 + k_3/K) \cdot [I^-]$  taking into account the equilibrium ( $K$ ):  $I_2 + I^- \rightleftharpoons I_3^-$

The experimental results taken from Table 4 can be used to calculate the value of  $k_2/K$  and of  $k_1 + k_3/K$  for tetramethyl- and tetraethyllead.

TABLE 4

IODOMETALLATION OF TETRAALKYLLEADS IN ACETONITRILE AT 365 m $\mu^a$ 

<i>M</i>	$[M] \cdot 10^2$	$[NaI]$	$D_0$	$[NaClO_4]$	$k_{\text{exp}}$ at 20 <sup>ob</sup> (l·mole <sup>-1</sup> ·sec <sup>-1</sup> )
Me <sub>4</sub> Pb	0.809	0.0103	2.95	0.0897	0.89 (0.91)
	1.45	0.0201	3.79	0.0799	0.50 (0.50)
	3.70	0.0505	2.80	0.0495	0.22 (0.21)
	7.30	0.100	3.71	0	0.116 (0.115)
	1.15	0.010	3.70	0	(0.84)
Et <sub>4</sub> Pb	0.70	0.0102	2.45	0.0898	(0.50)
	1.57	0.0205	2.15	0.0795	(0.276)
	3.04	0.0507	1.75	0.0493	(0.107)
	2.92	0.100	3.30	0	(0.058)
	6.20	0.100	2.30	0	(0.058)

<sup>a</sup> We did not determine the value of  $\epsilon(I_3^-)$  in MeCN, because all the kinetics in that solvent were cleanly pseudo-monomolecular. <sup>b</sup> The results given in parentheses were obtained graphically.

One can easily show that  $k_{\text{exp}}(\text{Me})/k_{\text{exp}}(\text{Et})$  is a function of  $[I^-]$

$$k_{\text{exp}}(\text{Me})/k_{\text{exp}}(\text{Et}) = k_2(\text{Me})/k_2(\text{Et}) \frac{1 + r_a(\text{Me}) \cdot [I^-]}{1 + r_a(\text{Et}) \cdot [I^-]} \text{ where } r_a = \frac{(k_1 + k_3/K)}{k_2/K}$$

By using the results quoted in Table 5, eqn. (4) gives the value of the polarity of acetonitrile in the absence of iodide ions:  $X(\text{MeCN}) = 0.04$ .

TABLE 5

VALUES OF  $k_2/K^a$  AND  $k_1 + k_3/K$  FOR THE REACTION BETWEEN TETRAALKYLLEADS AND IODINE IN MeCN·I<sup>-</sup>

	Me <sub>4</sub> Pb	Et <sub>4</sub> Pb
$k_2/K^a$	0.0090	0.0050
$k_1 + k_3/K^a$	0.029	0.008

<sup>a</sup> Another series of experiments made in 1963 gave

$$k_{\text{exp}}(\text{Me}) \cdot [I^-] = 0.0054 + 0.03 [I^-]$$

and

$$k_{\text{exp}}(\text{Et}) \cdot [I^-] = 0.030 + 0.008 [I^-]$$

The runs made in 1965 lead to different values for  $k_2/K$ , but the ratio  $k_{\text{exp}}(\text{Me})/k_{\text{exp}}(\text{Et})$ , which is the only quantity we discuss, is identical when taking the earlier or the latest results. We cannot see the reason for these differences in the experimental rate constants.

This shows that acetonitrile is a solvent of the same polarity as acetic acid in the absence of iodide ions. The presence of iodide ions in that solvent seems to increase its "polarity" when the ionic strength is kept constant.

## DISCUSSION

The similarity between the results of the reaction of tetraalkyltins with iodine<sup>7</sup> with those for the same reaction of tetraalkylleads suggests a similarity of the mechanisms, as do the identical values obtained for  $X$  (DMSO) by studying either reaction.

The decrease of the selectivity observed for the alkyllead compounds is best explained by the increased reactivity of these compounds towards halogens.

The presence of a term  $k_1 + k_3/K$  in  $k_{\text{exp}}(\text{MeCN})$  shows that the transition state for that part of the reaction includes an iodide ion, and its formula should be  $\text{PbR}_4 \cdot \text{I}_2 \cdot \text{I}^-$ ; this transition state may be pictured in at least three different ways: (a) "nucleophilic assistance"<sup>13</sup>; (b) attack on carbon by the weaker electrophile  $\text{I}_3^-$ , present in larger concentration; (c) by an intermediate structure.

It is indeed difficult to attribute the influence of  $[\text{I}^-]$  on  $k_{\text{exp}}$  to a partial ionisation of NaI in acetonitrile because this influence is different on  $\text{Et}_4\text{Pb}$  and on  $\text{Me}_4\text{Pb}$ .

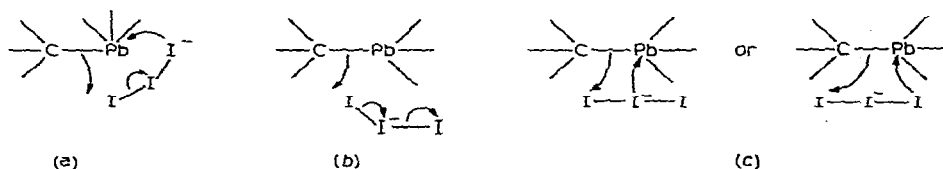
In order to try to decide between nucleophilic assistance and attack by  $\text{I}_3^-$ ,

TABLE 6

COUPLING CONSTANTS  $\Delta J = J(^{117}\text{Sn}-\text{C}-\text{H}) - 55.0^\circ$  OR  $J(^{119}\text{Sn}-\text{C}-\text{H}) - 57.8^\circ$  OF TRIMETHYL TIN BROMIDE IN THE PRESENCE OF HALIDE IONS IN DIFFERENT SOLVENTS

Solvent	$[\text{Me}_3\text{SnBr}]$	$\text{MX}$	$[\text{MX}]$	$\Delta J$ (cps) <sup>7</sup>
DMSO	0.4	—	—	11.9
	0.4	NaI	1 M	11.7
	0.4	LiBr	1 M	13.1
	0.4	LiCl	1 M	15.2
DMF	0.5	—	—	11.9
	0.5	LiBr	1 M	11.9
MeOH	0.5	—	—	9.5
	0.5	NaI	1 M	9.5
	0.5	NaBr	1 M	9.6
AcOH	0.5	—	—	3.8
	0.5	LiI	1 M	5.2
	0.5	LiBr	1 M	6.4
	0.5	LiCl	1 M	7.2
MeCN	0.33	—	—	6.2
	0.33	NaI	0.1 M	7.2
	0.33	NaI	1 M	8.3
	0.33	LiBr	1 M	12.6
	0.33	NaClO <sub>4</sub>	1 M	6.2
Me <sub>2</sub> CO	0.5	—	—	7.0
	0.58	NaI	0.07 M	7.8
	0.46	NaI	0.25 M	9.4
	0.42	NaI	0.5 M	10.4
	0.52	NaI	1 M	11.2
	0.5	LiBr	1 M	14.7
	0.5	LiCl	1 M	15.3

<sup>7</sup> 55.0 and 57.8 are the coupling constants for  $\text{Me}_3\text{SnBr}$  in  $\text{CCl}_4$ .



the influence of the solvent on the complexation of  $\text{Me}_3\text{SnBr}$  by halide ions (as nucleophiles) has been examined by NMR.

TABLE 7

PARALLEL BETWEEN THE EFFECT OF  $\text{X}^-$  ON KINETICS AND COMPLEXATION

Solvent	Kinetics	NMR
DMSO	no assistance by $\text{I}^-$ <sup>a</sup>	no complexation by $\text{I}^-$
DMF	no assistance by $\text{Br}^-$ <sup>15</sup>	no complexation by $\text{Br}^-$
MeOH	no assistance by $\text{I}^-$ <sup>a</sup>	no complexation by $\text{I}^-$
AcOH	(assistance by $\text{I}^-$ ?)	complexation by $\text{I}^-$
$\text{Me}_2\text{CO}$	assistance by $\text{I}^-$ <sup>12,b</sup>	complexation by $\text{I}^-$
MeCN	assistance by $\text{I}^-$ <sup>16,a,c</sup>	complexation by $\text{I}^-$

<sup>a</sup> This work. <sup>b</sup> Iododemetalation of tetraallyllead in acetone, which is described by  $v = k_{\text{exp}} \cdot [\text{M}] \cdot [\text{I}_3^-]$ , has a rate constant dependent on the iodide concentration  $k_{\text{exp}} \cdot [\text{I}^-] = 1.05 + 2 [\text{I}^-]$ . <sup>c</sup>  $\text{R}-\text{C}_6\text{H}_4-\text{SnMe}_3$  reacts with iodine in acetonitrile in the presence of iodide ions and the rate of the reaction depends on  $[\text{I}^-]$ :

$$\begin{array}{ll} \text{for R = H} & k_2/K = 5 \cdot 10^{-5} \quad \text{and} \quad k_3/K + k_1 = 0.01 \\ \text{for R = } p\text{-Br} & k_2/K = 1.8 \cdot 10^{-5} \quad \text{and} \quad k_3/K + k_1 = 0.01 \\ \text{for R = } p\text{-OMe} & k_2/K = 8.2 \cdot 10^{-3} \quad \text{and} \quad k_3/K + k_1 = 0.032 \end{array}$$

We may now establish an interesting parallel (see Table 7) between the ability of complexation of  $\text{Me}_3\text{SnBr}$  by  $\text{X}^-$  on one hand and the influence of the same  $\text{X}^-$  on  $k_{\text{exp}} \cdot [\text{X}^-]$  measured kinetically for the reactions of alkylated tin and lead derivatives with halogens  $\text{X}_2$  on the other hand.

Another parallelism will give us some complementary informations concerning the transition state of the iododemetalation of tetraalkyllead<sup>3</sup>.

Table 8 shows the results of some aromatic and aliphatic electrophilic substitutions in methanol.

It shows clearly that, in the case of aromatic electrophilic substitution, the nature of the metal has only a relatively small influence on the reaction rate, contrary to the case of electrophilic aliphatic substitution.

TABLE 8

KINETIC RESULTS FOR THE REACTIONS OF ORGANOLEAD AND ORGANOTIN COMPOUNDS WITH IODINE IN METHANOL

$S_E(\text{Aryl})$		$S_E(\text{Alkyl})$	
Compound	$k_2$	Compound	$k_2$
$\text{Me}_3\text{Pb}-\text{C}_6\text{H}_5^a$	69,000	$\text{Me}_4\text{Pb}$	10,800
$\text{Me}_3\text{Sn}-\text{C}_6\text{H}_5^a$	980	$\text{Me}_4\text{Sn}$	6.8

<sup>a</sup> The value for  $\text{Me}_3\text{Pb}-\text{C}_6\text{H}_5$  found by Buchman *et al.*<sup>14</sup> differs from that found by Delhaye *et al.*<sup>14</sup>; the present result has been obtained from very careful measurements by P. Launois<sup>14</sup>.

One may conclude that, for aliphatic electrophilic substitution, the important factor is bond-breaking. Now, for the same reaction with tetraalkyltins, bond-breaking is also an important factor<sup>6</sup>. This is yet another similarity between the iododemetalation of tetraalkylleads and -tins.

#### ACKNOWLEDGEMENTS

The authors are much indebted to Prof. R. H. MARTIN for valuable suggestions and stimulating interest. They wish to express their gratitude to Miss N. DEFAY and to Mr. R. POLAIN for helpful discussions and for recording the NMR spectra. The financial support of the Fonds National de la Recherche Scientifique (F.N.R.S.) is gratefully acknowledged. Thanks are due to Dr. G. M. VAN DER WANT and his collaborators (Institute for Organic Chemistry TNO, Utrecht, Holland) for their generous gift of tetraethyllead samples.

#### SUMMARY

The very similar sensitivity of the iododemetalation of tetraalkyltins and -leads to solvent effects suggests close similarity between the mechanisms of cleavage of C-Sn and C-Pb bonds; bond-breaking seems to be the rate-determining factor. The importance of nucleophilic assistance in this type of reactions is emphasized.

#### REFERENCES

- 1 G. TAGLIAVINI, S. FALESCHINI, G. PILLONI AND G. PLAZZOGNA, *J. Organometal. Chem.*, 5 (1966) 136.
- 2 L. RICCOBONI, G. PILLONI, G. PLAZZOGNA AND G. TAGLIAVINI, *J. Electroanal. Chem.*, 11 (1966) 340.
- 3 M. GIELEN, Mémoire de Licence, U.L.B., Brussels, 1960.
- 4 G. C. ROBINSON, *J. Org. Chem.*, 28 (1963) 843.
- 5 M. GIELEN, J. NASIELSKI, J. E. DUBOIS AND P. FRESNET, *Bull. Soc. Chim. Belges*, 73 (1964) 293.
- 6 S. BOUE, THESIS, U.L.B., Brussels, 1966; S. BOUE, M. GIELEN AND J. NASIELSKI, to be published.
- 7 M. GIELEN AND J. NASIELSKI, *J. Organometal. Chem.*, 1 (1963) 173.
- 8 J. C. JUNCERS, personal communication.
- 9 N. KORNBLUM, R. SELTZER AND P. HABERFIELD, *J. Am. Chem. Soc.*, 85 (1963) 1149.
- 10 P. BAEKELMANS, M. GIELEN AND J. NASIELSKI, *Ind. Chim. Belge*, 29 (1964) 1265.
- 11 M. GIELEN, *Ind. Chim. Belge*, 26 (1961) 216.
- 12 M. GIELEN AND J. NASIELSKI, *Bull. Soc. Chim. Belges*, 71 (1962) 32.
- 13 M. GIELEN AND N. SPRECHER, *Organometal. Chem. Rev.*, 1 (1966) 455.
- 14 O. BUCHMAN, M. GROSJEAN AND J. NASIELSKI, *Helv. Chim. Acta*, 47 (1964) 47; A. DELHAYE, J. NASIELSKI AND M. PLANCHON, *Bull. Soc. Chim. Belges*, 69 (1960) 134; P. LAUNOIS. Unpublished results.
- 15 M. GIELEN AND J. NASIELSKI, *Bull. Soc. Chim. Belges*, 71 (1962) 601.
- 16 J. MICHELET, Thesis, U.L.B., Brussels, 1965.

*J. Organometal. Chem.*, 7 (1967) 273-280